Bull. Environ. Contam. Toxicol. (1996) 57:l-7

Bulletin of Environmental Contamination and Toxicology

Variations of Volatile Chlorinated Hydrocarbons in Ambient Air at Industrial Areas in Niigata

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Received: 15 September 1995/Accepted: 1 February 1996

Typical volatile chlorinated hydrocarbons (VCHs), 1,1,1-trichloroethane (methyl chloroform, MCF), and trichloroethene (trichloroethylene, TCE) are used as degreasers or cleaners at electrical plants and metalworks; tetrachloroethene (perchloroethylene, PCE) as well as MCF is representative solvents for dry cleaning. Tetrachloromethane (perchloromethane, PCM) is utilized as material for chemicals. Some amounts of VCHs are lost in the process and are introduced to the environment by some routes. In particular, direct exhaust of VCHs into air is one of the most serious routes; 60 to 90 percents of the VCHs used at some metalworks and relative factories were estimated to be emitted into air (Kawata and Ozaki 1992, Kawata *et al.* 1992a, Kitajima *et al.* 1991).

We have previously reported the concentration levels of the VCHs in ambient air at some areas (Kawata *et al.* 1993, 1995); the atmospheric VCH concentrations at industrial areas were affected with some factories which used the VCHs, whereas those at a suburban area were lower than those at industrial regions. Furthermore, they were higher in winter season than in summer season, which might be caused by meteorological factors. In this paper, we present aerial variations of VCH concentrations during two to five years at three individual industrial areas, *i.e.,* a metalware and houseware manufacturing area, a textile and dyeing industrial area and a chemical engineering area.

MATERIALS AND METHODS

Concentrations of the four VCHs were studied in three industrial areas, Tsubame, Tokamachi and Kubiki in Niigata Prefecture. More than 200 factories are manufacturing metalware and houseware in Tsubame area. MCF and TCE have been used as degreasers by these factories in this area for several decades, MCF amounts used annually in this area were 200 - 250 tons during fiscal 1989 to 1991, 180 tons in 1992 and 60 tons in 1993, Nine hundred to a thousand tons of TCE had been used annually during the investigated period. In Tokamachi area, a number of dye works have been operated using MCF and PCE as solvents for dry cleaning in dyeing cloths. MCF amounts used were five to seven tons annually

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from fiscal 1989 to 1992 and 1.6 tons in 1993. PCE used were 60 to 80 tons annually. In Kubiki area, there are several chemical plants. While fifty tons of MCF was used as solvent in fiscal 1992, less than 1 ton of MCF was used in 1993. PCE of a few decade kg annually was also used as solvent. Thirteen to sixteen tons of PCM are synthesized annually at one of chemical plants. Samples were collected from April 1990 through March 1994 in Tsubame, from April 1989 through March 1994 in Tokamachi and from April 1992 to March 1994 in Kubiki. Samples were collected for a week twice a month in these sites.

Air pumps, NS-S2 (Niisei) and gas flow meters, DC-2 (Shinagawa) were used for sample collection. Mini pumps, TMP-6L (Toyo) were utilized for elution procedure. A gas chromatograph, GC-7A (Shimadzu), equipped with an electron capture detector was used for quantitative analysis. Activated carbon, Calgon BPL was ground into 35 to 60 mesh, and washed with carbon disulfide and then with methanol and with hexane for eight hr a solvent by using Soxhlet apparatus. The collection tube used was a glass column (115 mm length, 17 mm id. with 3 mm id. both edges) packed with 5 g of the activated carbon supported by small plugs of quartz wool. The tubes were preconditioned at 150°C for 24 hr with a nitrogen flow of 0.1 L/min (Kawata *et al.* 1992). Standards of the VCHs and other reagents were obtained from Wako.

Weekly mean concentrations of atmospheric VCH were measured by the following method (Kawata *et al.* 1992, Urano *et al.* 1992). Air was sampled with the collection tube at 0.1 L/min for a week (168 hr). The collected VCHs were eluted from the column with 50 ml of *n*-hexane at 0.5 ml/min. An aliquot of the eluate was analyzed by the gas chromatograph. The gas-chromatographic conditions were as follows: column; glass column (3 m X 3 mm id) packed with 20 % Silicone DC-200 on Chromosorb W AW-DMCS (60/80 mesh), carrier gas; nitrogen of 40 ml/min, temperatures of injector, column and detector; 2OO°C, 90°C and 200°C. The extraction efficiencies for spiked VCHs from the column were 87 - 98 %, and the collection efficiencies of the activated carbon column were 91 - 100 % as previously reported (Kawata *et al.* 1992, 1995).

RESULTS AND DISCUSSION

Concentrations of the four VCHs are summarized in Table 1. Aerial VCHs concentrations in industrial areas where the VCHs are used and/or synthesized are higher than those in the other areas. The mean concentrations of MCF in Tsubame (2.3 ppb) and Tokamachi (1.5 ppb) were almost comparable to those of 2.1 to 2.3 ppb at an industrial area in Yokohama, Japan (Urano *et al.* 1992). The mean concentration in Kubiki, 0.76 ppb is statistically significantly lower than those in Tsubame and Tokamachi. It was the same as the mean concentration (0.70 ppb) at a rural site in East St. Louis, Illinois (Sweet and Vermette 1992).

MCF has been regulated in synthesis and usage because it is regarded as a

responsible compound both for the stratospheric ozone depletion and the global warming. Accordingly, the amounts of MCF used were decreased from 200 - 250 tons to 180 tons in fiscal 1992 and 60 tons in 1993 in Tsubame, from five to seven tons annually to 1.6 tons in 1993 in Tokamachi, and from 50 tons in 1992 to <1 tons in 1993 in Kubiki. The aerial MCF concentrations in these areas were consequently decreased in fiscal 1992 to 1993 in Tsubame and in 1992 in Tokamachi and Kubiki (Table 1). Although MCF amount used in Tsubame had been about 30 to 40 times as many as those in Tokamachi, means of atmospheric MCF concentrations in Tsubame were only twice as high as those in fiscal 1990 - 1991 or almost same as those in 1992 - 1993 in Tokamachi. While MCF amount used in Tsubame in fiscal 1992 was about four times as many as that in Kubiki in the same year, MCF concentrations in both areas were almost same levels. This suggests that there had been differences in usage and disposition of the MCF at factories in these areas.

Table 1. VCH concentrations in industrial areas

Area	Year [a]	*n* [b]	Concentration [c] (ppb)							
			MCF		TCE		PCE		PCM	
Tsubame	1990	24	3.0	*2.7*	4.4	*3.8*	0.087	*0.078*	0.10	*0.10*
			(1.3 - 7.7)		(0.73 - 9.5)		(0.027 - 0.20)		(0.087 - 0.12)	
	1991	24	3.3	*2.7*	4.8	*4.4*	0.12	*0.10*	0.10	*0.10*
			(1.3 - 11)		(2.3 - 12)		(0.033 - 0.23)		(0.087 - 0.12)	
	1992	24	1.9	*1.8*	4.6	*4.0*	0.066	*0.063*	0.11	*0.11*
			(0.80 - 3.2)		(1.7 - 9.9)		(0.036 - 0.11)		(0.097 - 0.13)	
	1993	24	0.93	*0.86*	3.4	*3.0*	0.11	*0.087*	0.11	*0.11*
			(0.35 - 1.8)		(0.56 - 8.0)		(0.019 - 0.22)		(0.096 - 0.13)	
	Total	96	2.3	*1.8*	4.3	*3.8*	0.090	*0.081*	0.10	*0.10*
			(0.35 - 11)		(0.56 - 12)		(0.019 - 0.23)		(0.087 - 0.13)	
Tokamachi	1989	24	1.6	*1.4*	0.10	*0.081*	0.63	*0.54*	0.10	*0.10*
			(0.43 - 4.6)		(0.023 - 0.30)		(0.20 - 1.2)		(0.085 - 0.13)	
	1990	24	1.6	*1.4*	0.057	*0.048*	0.91	*0.85*	0.11	*0.11*
			(0.63 - 3.7)		(0.016 - 0.15)		(0.51 - 1.7)		(0.093 - 0.14)	
	1991	24	1.4	*1.3*	0.040	*0.031*	1.0	*0.90*	0.11	*0.11*
			(0.55 - 3.0)		(0.002 - 0.15)		(0.37 - 2.1)		(0.091 - 0.12)	
	1992	24	2.1	*1.5*	0.026	*0.021*	1.0	*0.90*	0.11	*0.11*
			(0.34 - 8.2)		(0.006 - 0.061)		(0.29 - 2.8)		(0.094 - 0.12)	
	1993	24	0.95	*0.83*	0.072	*0.057*	0.74	*0.67*	0.11	*0.11*
			(0.12 - 2.3)		(0.016 - 0.18)		(0.32 - 2.2)		(0.096 - 0.13)	
	Total	120	1.5	*1.2*	0.059	*0.042*	0.86	*0.76*	0.11	*0.11*
			(0.12 - 8.2)		(0.002 - 0.30)		(0.20 - 2.8)		(0.085 - 0.14)	
Kubiki	1992	24	1.1	*0.94*	0.059	*0.041*	0.22	*0.17*	0.21	*0.19*
			(0.32 - 2.0)		(0.007 - 0.19)		(0.05 - 0.63)		(0.11 - 0.47)	
	1993	24	0.48	*0.44*	0.079	*0.062*	0.15	*0.11*	0.17	*0.17*
			(0.20 - 1.1)		(0.010 - 0.23)		(0.024 - 0.40)		(0.11 - 0.28)	
	Total	48	0.76	*0.64*	0.069	*0.051*	0.18	*0.14*	0.19	*0.18*
			(0.20 - 2.0)		(0.007 - 0.23)		(0.024 - 0.63)		(0.11 - 0.47)	

[a] Fiscal year (April - March).

[b] Number of samples.

[c] Roman: arithmetic mean, *italic*: geometric mean, parentheses: minimum - maximum.

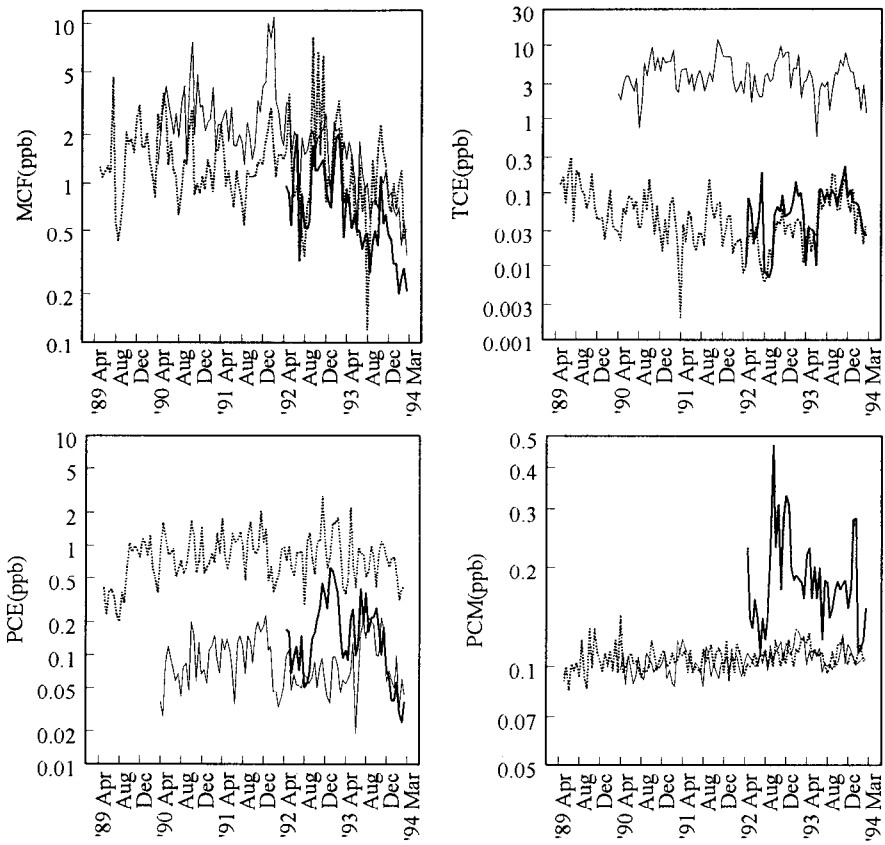

Figure 1. Variations of VCH concentrations in Tsubame (solid line), Tokamachi (dotted line) and Kubiki (thick solid line)

The mean TCE concentrations in Tokamachi (0.059 ppb) and Kubiki (0.069 ppb) were almost comparable to 0.097 ppb at a rural site in Okayama, Japan (Oda *et al.,* 1992). In contrast, TCE concentration in Tsubame is statistically significantly higher than those in the other area investigated. As mentioned already, as many as nine hundred to a thousand tons of TCE had been used annually in this area. The mean TCE concentration in Tsubame (4.3 ppb) was about a hundred times higher than those in the other areas and three to seven times higher than 0.59 - 1.5 ppb in the Yokohama industrial area, (Urano *et al.* 1992) and approached 6.6 ppb at an industrial site in Turke, Finland (Kroneld, 1989).

The mean concentration of PCE in Tsubame, 0.090 ppb was about two times higher than 0.048 ppb both in the Okayama rural area (Oda *et al.,* 1992) and the suburban area in Niigata (Kawata *et al.* 1995) or 0.058 ppb at a rural site in Illinois (Sweet and Vermette 1992). PCE concentration in Kubiki (0.18 ppb) was two times higher than that in Tsubame and a half of 0.36 ppb in Yokohama (Urano *et al.*

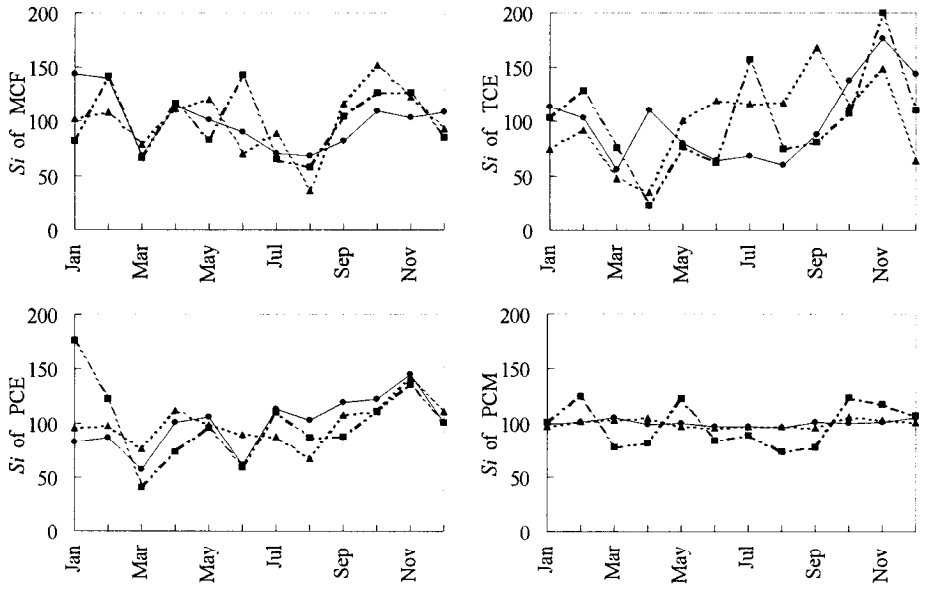

Figure 2. Monthly *Si* variations at Tsubame (●), Tokamachi (▲) and Kubiki (■)

1992). On the other hand, that in Tokamachi (0.86 ppb), where 60 to 80 tons of PCE has been used annually, was rather higher and significantly different from those in Tsubame and Kubiki; it was almost same as 0.64 - 0.82 ppb in industrial areas in Nagoya Japan (Urano *et al.* 1988).

The mean concentrations of PCM (0.10 - 0.11 ppb) in Tsubame and Tokamachi were the same as 0.10 ppb in the Niigata suburban area (Kawata *et al.* 1995) and 0.093 - 0.108 ppb at some unpolluted sites in Japan (Makide *et al.* 1979). However, PCM concentration in Kubiki, where PCM has been synthesized, was statistically significantly higher than those in the other two areas, It is comparable to the concentrations in some industrial areas; 0.20 - 0.23 ppb in Kawasaki, Japan (Urano *et al.* 1988) 0.24 ppb at Nakago, Niigata (Kawata and Fujieda 1993). This thought to be that a part of PCM synthesized were discharged to the air.

Variations of the individual four VCH concentrations in the ambient air are given in Figure 1. MCF, TCE and PCE concentrations show rather violent variations; the ratios *(R)* of the maximum concentration to the minimum one during the investigated periods (Table 1) were 10 - 68 for MCF, 21 - 150 for TCE and 12-26 for PCE. On the other hand, PCM concentration gives a relatively temperate variation; *R* values for PCM were only 1.5 - 4.3. These characteristic variations of the four VCHs were in the suburban area in Niigata (Kawata *et al.* 1995).

To evaluate monthly variation of each VCH, seasonal index, *Si,* for every month is calculated by equation:

$$Si = 100 \times M/Mo$$

Table 2. Correlation among *Si* values and meteorological factors

	Tsubame				Tokamachi				Kubiki			
	MCF	TCE	PCE	PCM	MCF	TCE	PCE	PCM	MCF	TCE	PCE	PCM
Air-temp.	*	-	-	**	-	**	-	*	-	-	-	-
Flux-of-global-solar-radiation	-	-	-	-	-	-	-	-	-	-	-	-
Duration-of-sunshine	-	*	-	-	-	-	-	-	-	-	-	-
Wind-speed	*	*	-	-	-	-	-	-	-	-	-	-

* $p<0.05$; ** $p<0.01$; - no significant correlation.

where *M* and *Mo* are geometric mean concentration in a month and total geometric mean concentration, respectively (Ueji 1986). Monthly variations of *Si* values are plotted in Figure 2. In case of the suburban area in Niigata, *Si* values of MCF, TCE and PCM showed common characteristic variations that they were higher in winter season than in summer season; monthly variation of *Si* seems to be caused mainly by meteorological factors, because they were significantly correlated with air temperature, flux of global solar radiation and duration of sunshine (Kawata *et al.* 1995). In contrast, *Si* values in the investigated industrial areas gave no common variations and there are no significant correlation except for the five cases (Table 2) suggesting the VCH concentrations might be caused by rather operation conditions of the industries located at each area than the meteorological factors. Moreover, Urano *et al.* [15] reported that VCH concentrations at a commercial area in Yokohama were in inverse proportion to wind speed. However, only MCF and TCE concentrations in Tsubame were correlated with wind speed in this study (Table 2).

REFERENCES

Kawata K, Fujieda Y (1993) Volatile chlorinated hydrocarbons in ambient air at Niigata area. Jpn J Toxicol Environ Hlth 39: 474-479

Kawata K, Kitajima E, Murayama H, Uemura T (1992a) Distribution of trichloroethylene in air, soil and groundwater around a metalware factory. Jpn J Toxicol Environ Health 38: 156- 161

Kawata K, Minagawa M, Yokoyama H, Fujieda Y (1992b) Evaluation of long-time adsorption methods for volatile chlorinated hydrocarbons in the atmosphere. J Environ Lab Assoc 17: 177- 181

Kawata K, Mukai H, Yasuhara A (1995) Variations of volatile chlorinated hydrocarbons in ambient air at a suburban area. Toxicol Environ Chem (in press)

Kawata K, Ozaki K (1992) Estimation of routes of volatile chlorinated hydrocarbons to the environment. Environ Sci 1: 109- 115

Kitajima E, Murayama H, Kobayashi T, Yago H (1991) Mass balance of trichloroethylene (TCE) in a hardware factory which installed TCE withdrawal device of exhaust gas. J Environ Chem 1: 553-557

Kroneld R (1989) Volatile pollutants in suburban and industrial air. Bull Environ Contam Toxicol 42: 868-872

Makide Y, Tominaga T, Rowland FS (1979) Gas chromatographic analysis of halocarbons in air over Japan. Chem Lett 355-358

Oda J, Maeda I, Ichikawa S (1992) Atmospheric concentration and behavior of volatile chlorinated hydrocarbons. J Environ Chem 2: 479-491

Simmond PG, Cunnold DM, Dollard GJ, Davies TJ, McCulloch A, Derwent RG (1993) Evidence of the phase-out of CFC use in Europe over the period 1987 - 1990. Atmos Environ 27A: 1397-1407

Sweet CW, Vermette SJ (1992) Toxic volatile organic compounds in urban air in Illinois. Environ Sci Technol 26: 165-173

Ueji T (1986) Time series Analysis in Economic Phenomena. In: Applied Statistical Handbook, Yokendo, Tokyo, pp.465-477

Urano K, Kawamoto K, Abe Y, Otake M (1988) Chlorinated organic compounds in urban air of Japan. Sci Total Environ 74: 121 - 131

Urano K, Miyamoto K, Okuyama K, Fujie K (1992) Halocarbons and aromatic hydrocarbons in urban air in Japan. J Jpn Soc Air Pollut 27: 227-236